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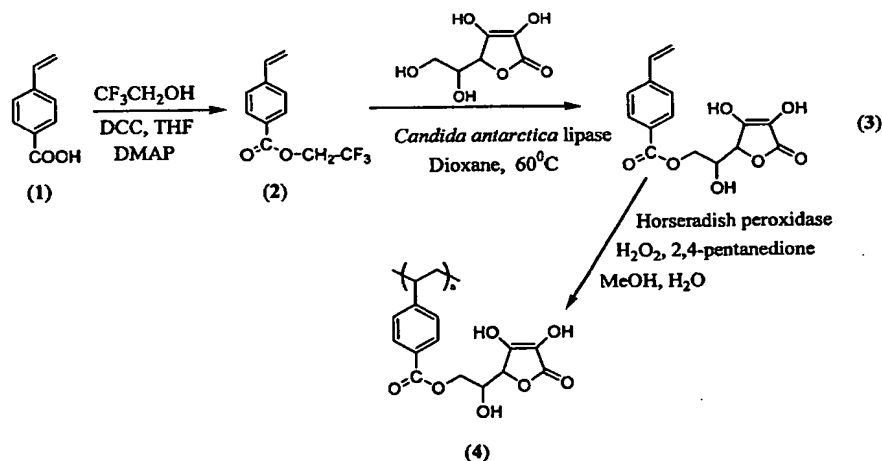
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[Continued on next page]

(54) Title: ANTIOXIDANT-FUNCTIONALIZED POLYMERS



(57) Abstract: Methods and compositions are disclosed for the preparation of free radical scavenging polymers and polymer films functionalized with antioxidants. Enzymatic and chemical tailoring of monomers with antioxidants followed by enzymatic polymerization is described. These antioxidant functionalized polymers can increase shelf life and quality of food products, as well as, increase effectiveness of pharmaceutical agents when used as packaging or as coatings on packaging for oxygen sensitive materials. The novel enzymatic covalent coupling of antioxidants to a polymer enhances the free radical scavenging ability of packaging while also inhibiting the escape of the antioxidants, and thus limiting exposure and/or absorption by an individual. In addition to its use in food or pharmaceutical packaging, methods are disclosed for using the antioxidant coupled polymers in a variety of applications including as coatings on the inside of medical devices, such as stents and catheters, which would substantially reduce free radical damage and/or oxygen depletion during medical procedures. Furthermore, through the coupling of antioxidants to biodegradable polymers, controlled delivery and sustained release of an antioxidant to a subject is possible.



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/37775

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K15/06 C12P17/00 A61F2/00 A61M1/00 A61M5/00
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K A61F A61M A61K C07D C08F C08G C12P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 23 March 2003 (2003-03-23), SINGH, AMARJIT ET AL: "Enzymatic approach to ascorbic acid-modified polymers for free radical scavenging" XP002277047 retrieved from STN Database accession no. 138:385828 abstract & POLYMERIC MATERIALS SCIENCE AND ENGINEERING (2003), 88, 308-309, ----- -/--</p>	1-18

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KOBAYASHI S ET AL: "ENZYMATIC POLYMERIZATION" CHEMICAL REVIEWS, AMERICAN CHEMICAL SOCIETY, EASTON, US, VOL. 101, PAGE(S) 3793-3818 , XP001121958 ISSN: 0009-2665 page 3797 -----	1-18
A	GILICK; KUCZKOWSKI: "POLYMER-BOUND ANTIOXIDANT" RUBBER CHEMICAL TECHNOLOGY, vol. 57, no. 3, 1984, pages 621-651, XP009029436 the whole document -----	1-18
A	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 20 November 2002 (2002-11-20), SINGH, AMARJIT ET AL: "Enzyme-based vinyl polymerization" XP002277176 retrieved from STN Database accession no. 138:188089 abstract & JOURNAL OF POLYMERS AND THE ENVIRONMENT (2002), 10(3), 85-91, -----	1-18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/37775

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 18

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-18

Method for enzymatically synthesizing a functionalised polymer whereby the resultant functionalised polymer has inherent antioxidant capabilities.

2. claims: 19-40

Method of protecting an oxygen sensitive material from degradation.

3. claims: 41-53

Medical device having at least a surface coated with a polymer comprising monomeric units functionalized with an antioxidant.

4. claims: 54-66

An antioxidant coupled packaging material

5. claims: 67-114

A controlled delivery system (claim 67), a method of controlled delivery (claim 84) and an ointment for controlled delivery of antioxidants (claim 102).

6. claims: 115-118

An ascorbyl coupled polymer
